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ORGANOTIN BIOCIDES

IX *. TRIORGANOTIN PHOSPHORODIAMIDATES

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Summary

Three triorganotin derivatives of *N,N'*-diphenylphosphorodiamidic acid and three further derivatives of *N,N,N',N'*-tetraethylphosphorodiamidic acid have been prepared and characterised by spectroscopic methods. Soluble derivatives are assigned cyclic, oligomeric structures, while insoluble triphenyltin compounds are believed to be chain polymers. Variable-temperature ^{119}Sn Mössbauer spectroscopy is used to assess the three-dimensional structure of these latter polymers.

Introduction

Organophosphorus compounds are the single most important group of insecticides, accounting for almost 20% of the insecticides in use in 1972 [2]. Their effectiveness results from bonding to acetylcholinesterase, an enzyme regulating the rate of hydrolysis of acetylcholine, thereby leading to uncontrolled hydrolysis and breakdown of the nervous system [3]. The biocidal nature of organotin derivatives [4] has prompted the synthesis of a number of derivatives of organophosphorus ligands, and several of such compounds e.g. (cyclo-$C_6H_{11})_3SnS_2P(OC_3H_7)_2$ are currently under patent [5]. Our own interest in these systems is well established and we have outlined the structural trends which underlie the organotin derivatives of oxy- and thiophosphorus acids [6]. In this report we contribute further to our understanding of these systems by reporting the synthesis and structural characterisation of organotin derivatives of two phosphorodiamidic acids, namely

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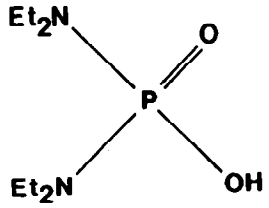
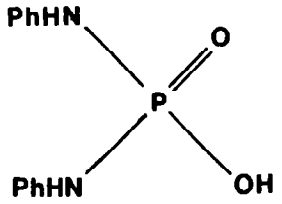
N,N,N',N'-tetraethyl- and *N,N'*-diphenylphosphorodiamidic acid (HTEPA (I), HDPPA (II), respectively).



(I)



(II)

Triphenyltin derivatives of I and the tributyltin ester of II have been prepared previously by Kubo [7] who found these compounds to be fungicidally active and slightly phytotoxic, but without pesticidal activity.

Experimental

Infrared spectra were recorded as KBr discs on a Perkin–Elmer 599B spectrophotometer. NMR and mass spectral data were collected on Hitachi/Perkin–Elmer R24B and V.G 70-70E instruments. Details of our Mössbauer spectrometer and related procedures have been described elsewhere [8]. *N,N'*-Diphenylphosphorodiamidic chloride was prepared by the method of Cook et al. [9] from aniline and phosphorus oxychloride. It was subsequently converted to the corresponding acid II by using KOH in methyl ethyl ketone [7]. *N,N,N',N'*-Tetraethylphosphorodiamidic chloride was prepared by the method of Kubo [7] and was purified by distillation. The synthesis of organotin derivatives of ligands I and II is typified by the following two examples. Additional preparative and full analytical data are given in Table 1.

Synthesis of O-(triphenylstannyl)-N,N'-diphenylphosphorodiamidate

Method A. II (1.35 g, 5.4 mmol) was added to a solution of Ph_3SnOH (2.00 g, 5.4 mmol) in hot toluene (80 cm^3). The reaction was refluxed for 2 h, and water formed during the course of the reaction removed using a Dean and Stark trap. The solution was filtered hot, and allowed to cool yielding the product (2.20 g, 60%) as a precipitate, essentially insoluble in organic solvents but analytically pure as collected.

Synthesis of O-(trimethylstannyl)-N,N'-diphenylphosphorodiamidate

Method B. To a suspension of $(PhNH)_2P(O)Cl$ (1.74 g, 6.5 mmol) in water (30 cm^3) was added a solution of KOH (0.80 g, 14.5 mmol) in water (5 cm^3). The

TABLE 1

PREPARATIVE AND ANALYTICAL DATA FOR ORGANOTIN PHOSPHORODIAMIDATES

Compound	Method	Yield (%)	M.p. (°C)	Analysis (Found (calcd.) (%))		
				C	H	N
$Ph_3Sn(TEPA)$	B [a]	65	> 235 (dec.) [b]	55.10 (56.04)	6.40 (6.33)	4.90 (5.03)
$Bu_3Sn(TEPA)$	B [c,d]	56	154–155 [e]	48.23 (48.31)	9.51 (9.51)	5.50 (5.63)
$Me_3Sn(TEPA)$	B [f]	55	> 230 (dec.)	35.52 (35.61)	7.75 (7.88)	7.51 (7.55)
$Ph_3Sn(DPPA)$	A	60	228–230 [g]	59.30 (60.33)	4.70 (4.56)	4.69 (4.69)
$Cy_3Sn(DPPA)$	A [d]	57	204–208 (dec.)	59.30 (58.56)	7.50 (7.37)	4.54 (4.55)
$Me_3Sn(DPPA)$	B [d]	83	180–182	43.91 (43.83)	5.28 (5.15)	6.88 (6.81)

[a] Reaction carried out in H_2O/acetone; product insoluble in organic solvents. [b] Lit. m.p. > 250°C [7]. [c] Reaction carried out in H_2O/EtOH. [d] Recrystallisation from EtOH. [e] Lit. m.p. 151–153°C [7]. [f] Recrystallisation from EtOH/Et_2O. [g] Lit. m.p. 187–89°C [7].

mixture was heated gently and stirred for 10 min, then left to stand overnight. To the aqueous solution of $(PhNH)_2PO_2K$ thus generated was added Me_3SnCl (1.30 g, 5.4 mmol) in water (40 cm^3) with vigorous stirring. The product precipitated as a white solid, which was filtered off after 30 min stirring and recrystallised from ethanol (2.14 g, 83%).

Results and discussion

Triorganotin derivatives of phosphorodiamidic acids I and II are prepared by either the azeotropic dehydration of toluene solutions containing the free acid and triorganotin hydroxide (eq. 1) or by metathesis of a triorganotin halide and a potassium salt of the acid (eq. 2).

$$R_3SnOH + (PhNH)_2PO_2H \rightarrow R_3SnO_2P(HNPh)_2 + H_2O \quad (1)$$

$(R = C_6H_5, \text{cyclo-}C_6H_{11})$

$$R_3SnCl + (R'R''N)_2PO_2K \rightarrow R_3SnO_2P(NR'R'')_2 + KCl \quad (2)$$

$(R = CH_3;\ R' = C_6H_5,\ R'' = H;$

$R = CH_3, \text{n-}C_4H_9, C_6H_5;\ R' = R'' = C_2H_5)$

The products are white crystalline solids which, apart from the two triphenyltin derivatives, are soluble in common organic solvents.

Mass spectra (Table 2) confirm the composition of the products and in most cases parent ions are observable. The spectra show fragments typical of organotins, with even-electron ions dominant as now appears the norm [10,11]. However, in the case of $Cy_3Sn(DPPA)$, rather surprisingly two odd-electron fragments $[H_2(C_6H_{11})SnO_2P(HNC_6H_5)_2^{+\cdot}$ and $(C_6H_{11})_2Sn^{+\cdot}]$ dominate the spectrum. In the case of $Me_3Sn(DPPA)$, a low abundance fragment is observed at *m/e* 561 showing the typical isotopic distribution pattern for Sn_2 and can be tentatively assigned to the

TABLE 2

70 eV MASS SPECTRA OF TRIORGANOTIN PHOSPHORODIAMIDATES [a]

Me_3Sn(DPPA)	561(0.8%, $Me_3SnOP(NHPh)_2OSnMe - H^+$), 412 (28, $Me_3SnO_2P(NHPh)_2^+$), 397 (100, $Me_2SnO_2P(NHPh)_2^+$), 304 (43, $Me_2SnO_2PNPh^+$), 289 (6, $MeSnO_2PNPh^+$), 274 (8, SnO_2PNPh^+), 242 (17, $Me_2SnO_2PN_2H^+$), 212 (24, $SnO_2PN_2H^+$), 185 (30, $SnO_2PH_2^+$), 165 (73, Me_3Sn^+), 150 (15, Me_2Sn^+), 135 (22, $MeSn^+$), 120 (12, Sn^+)
Ph_3Sn(DPPA)	351 (25, Ph_3Sn^+), 197 (8, $PhSn^+$), 154 (47, Ph_2^+), 120 (4, Sn^+)
Cy_3Sn(DPPA)	452 (81, $H_2CySnO_2P(NHPh)_2^+$), 369 (2, Cy_3Sn^+), 367 (5, $SnO_2P(NHPh)_2^+$), 365 (7, $Cy_2SnO_2PNH_2^+$), 331 (3, $Cy_2SnOP-2H^+$), 286 (80, Cy_2Sn^+), 203 (16, $CySn^+$), 121 (10, SnH^+), 120 (6, Sn^+)
Me_3Sn(TEPA)	372 (8, $Me_3SnO_2P(NEt_2)_2^+$), 357 (28, $Me_2SnO_2P(NEt_2)_2$) [b], 343 (2, $Me_3SnO_2P(NEt_2)(NEt^+)$ 300 (28, $Me_3SnO_2PNEt_2^+$), 286 (23, $Me_3SnO_2PNEtMe^+$), 165 (42, Me_3Sn^+), 150 (8, Me_2Sn^+), 135 (8, $MeSn^+$), 120 (2, Sn^+)
Ph_3Sn(TEPA)	558 (7, $Ph_3SnO_2P(NEt_2)_2^+$), 543 (5, $Ph_3SnO_2P(NEt_2)(NEtCH_2)^+$), 527 (2, $Ph_3SnO_2P(NEt_2)(NEt)^+$), 481, (67, $Ph_2SnO_2P(NEt_2)_2^+$), 408 (8, $Ph_2SnO_2PNEt_2 - H^+$), 351 (31, Ph_3Sn^+), 332 (22, $PhSnO_2PNEt_2^+$), 275 (11, Ph_2SnH^+), 197 (28, $PhSn^+$), 120 (10, Sn^+)
Bu_3Sn(TEPA)	441 (100, $Bu_2SnO_2P(NEt_2)_2^+$), 370 (38, $Bu_2SnO_2PNHEt_2^+$), 327 (12, $SnO_2P(NEt_2)_2^+$), 291 (4, Bu_3Sn^+), 256 (16, $SnO_2PNHEt_2^+$) 235 (6, Bu_2SnH^+), 177 (17, $BuSn^+$), 121 (6, SnH^+)

[a] Based upon ^{120}Sn, ^{31}P, ^{16}O, ^{14}N, ^{12}C, ^{1}H. [b] Alternatively $Me_3SnO_2P(NEt_2)(NEtCH_2)^+$.

species $[(Me_3Sn)_2O_2P(HNPh)_2 - H]^+$. Such observations are suggestive of an associated solid state structure which retains a portion of its integrity in the gaseous phase conditions prevailing within the mass spectrometer. The absence of similar ditin fragments in other spectra cannot, however, be taken as evidence against lattice association in these cases.

Infrared data for selected bands in the derivatives of HDPPA and HTEPA are given in Table 3. The low frequency ν(N–H) in the unmetallated HDPPA has been considered indicative of a zwitterionic form ($RN^+H_2PO_2^-$) for many phosphoroamidates [12]. However, a sharp ν(O–H) band at 3365 cm^{-1} is found in the spectrum of the acid discounting such a structure, and instead the low frequency ν(N–H) can be attributed to N–H $\cdots$ O=P hydrogen bonding within the solid lattice. This structure is disrupted when the ligand is bonded to a metal moiety, as evidenced by a shift in ν(N–H) to higher frequency (ca. 3400 cm^{-1}) seen in the spectra of all the triorganotin phosphorodiamidates studied. The absence of ν(O–H) and ν(P–OH) bands in these derivatives is consistent with the expected bonding to tin via oxygen.

Information concerning the metal–oxyphosphorus ligand bonding can be obtained from considerations of $\nu_{asym}(PO_2)$. In derivatives of I (1145–1110 cm^{-1}) and II (1150–1145 cm^{-1}) this band is at lower frequencies than the parent compound II (1215 cm^{-1}), and although such comparisons are not directly valid for derivatives of I the data appear consistent with bidentate ligand behaviour and a strong secondary P=O: $\rightarrow$ Sn bond. Similar values for $\nu_{asym}(PO_2)$ have been observed in other phosphorus ligands [13–15] and in each case this has been considered as evidence for bidentate ligand behaviour. Furthermore, solution state infrared spectra for the four soluble triorganotin phosphorodiamidates show that $\nu_{asym}(PO_2)$ is essentially

TABLE 3

SELECTED INFRARED DATA [a] FOR ORGANOTIN PHOSPHORODIAMIDATES [b]

Assignment	$(PhNH)_2PO_2H$	$(Et_2N)_2P(O)Cl$	$Ph_3Sn(DPPA)$	$Cy_3Sn(DPPA)$	$Me_3Sn(DPPA)$	$Ph_3Sn(TEPA)$	$Bu_3Sn(TEPA)$	$Me_3Sn(TEPA)$
ν(O–H)	3365m							
ν(N–H)	3320,3150m,br		3360m	3430,3440m	3410,3390m			
				(3420m)	(3400m)			
ν(P=O)		1250s						
$\nu_{asym}(PO_2)$	1215s		1150s	1175s	1160s	1110s	1135s	1145s
				(1170s)	(1160s)		(1155,1140s)	(1150s)
$\nu_{sym}(PO_2)$	980s		1070s	1060s	1070s	1025s	1050s	1050s
				(1065m)	(1060s)		(1050s)	(1050s)
ν(P–OH)	960s							
ν(P–N–C)	920s		930s	930s	930s			
ν_{asym}(Sn–C)					552m			550s [d]
$\delta(PO_2)$	460m		455m	420vw	450vw	460m	460sh	470sh

[a] ± 3 cm^{-1}. [b] KBr disc; solution spectra ($CHCl_3$) in parentheses. [c] Bands associated with the Et_2N-P group have also been found to occur at 1170 and 1025 cm^{-1} [12]. [d] Raman: 550m, 514s.

TABLE 4

^{1}H NMR DATA FOR TRIORGANOTIN PHOSPHORODIAMIDATES [a]

Compound	Chemical shift	$^2J(^{31}P-N-^1H)$	$^3J(^{31}P-NC-^1H)$	$^2J(^{119}Sn-C-^1H)$
$Me_3Sn(DPPA)$	CH_3-Sn; 0.50s			72
	N*H*; 4.62d	8		
	Ph; 6.80m			
$Me_3Sn(DPPA)$ [b]	CH_3; 0.52s	8		72
	N*H*; 6.10d			
	Ph, 6.77m			
$Cy_3Sn(DPPA)$	$-CH_2$; 1.80m			
	N*H*; 5.18d	8		
	Ph; 6.98m			
$Me_3Sn(TEPA)$	CH_3Sn; 0.43 s			74
	CH_3; 0.98t			
	$-CH_2$-; 2.78m		10.5	
$(Et_2N)_2P(O)Cl$	CH_3; 1.11t			
	CH_2; 3.05m		14	

[a] Shifts relative to Me_4Si (ppm); coupling constants in Hz. All data recorded as $CDCl_3$ solutions, unless stated otherwise. [b] Acetone-d_6 solution.

unaffected by dissolution, ruling out polymeric structures whose bridges would be disrupted in solution. The bonding within the PO_2Sn unit must therefore rest between a chelating ligand with a *cis*-O_2SnR_3 geometry at tin, or bridging, bidentate ligand behaviour centred on a *trans*-O_2SnR_3 configuration about the metal within the context of a cyclic, oligomeric structure. In principle, such structures can be distinguished when R = CH_3 from the pattern of $\nu_{sym,asym}$(Sn–C) vibrations. In the case of Me_3Sn(TEPA) and Me_3Sn(DPPA) the issue is somewhat clouded by the occurrence of presumably ligand-related bands of medium intensity at 530, 505 cm^{-1} found in the spectra of all the compounds studied, thus obscuring detail in the 500–550 cm^{-1} region of the spectrum where such Sn–C vibrations are known to occur. For both trimethyltin compounds, a strong ν_{asym}(Sn–C) is clearly seen at ca. 550 cm^{-1}. In the Raman spectrum of Me_3Sn(TEPA) a strong band occurs at 514 cm^{-1} which is absent in the infrared spectrum and is assignable to ν_{sym}(Sn–C). The ν_{asym}(Sn–C) at 550 cm^{-1} is still visible in the Raman spectrum, but is markedly diminished in intensity. Unfortunately Me_3Sn(DPPA) decomposes in the laser beam, however we interpret the available collective spectral findings for both compounds as arising from a near-planar [SnC_3] moiety, and is supportive of the cyclic oligomeric structure suggested above. ν_{sym}(Sn–C) have been observed at 519 and 500 cm^{-1} in the Raman spectra of $Me_3SnO_2PPh_2$ [15] and $Me_3SnO_2PMe_2$ [13], respectively.

In addition to confirming the composition of the reaction products, ^{1}H NMR data (Table 4) can also provide evidence for the configuration of SnC_3 skeleton in trimethyltin compounds from the magnitude of $^2J(^{119}Sn-C-^1H)$. For both trimethyltin derivatives the magnitude of this coupling in $CDCl_3$ is 72 Hz and is independent of concentration. Moreover, in the coordinating solvent acetone the coupling remains unchanged although δ(N*H*) does show a downfield shift, possibly due to hydrogen bonding with the donor solvent. These data are similar to those for

TABLE 5

^{119}Sn MÖSSBAUER SPECTROSCOPIC DATA (78 K) FOR ORGANOTIN PHOSPHORODIAMIDATES [a]

Compound	*IS* [b]	*QS* [c]	$\Gamma_{1,2}$ [d]	10^2a (K^{-1})	*r* (*T* range; pts) [e]
Ph_3Sn(DPPA)	1.27	3.38	0.90, 0.86	1.84	−0.998 (78–130 K; 8)
Cy_3Sn(DPPA)	1.58	3.91	0.91, 0.90		
Me_3Sn(DPPA)	1.30	3.73	0.86, 0.81	2.11	−0.999 (78–130 K; 8)
Ph_3Sn(TEPA)	1.23	3.35	0.91, 0.88	1.33	−0.998 (78–130 K; 8)
Bu_3Sn(TEPA)	1.41	3.68	0.86, 0.85		
Me_3Sn(TEPA)	1.30	3.43	0.92, 0.84		

[a] All values in mm s^{-1}. [b] ±0.02 mm s^{-1}. [c] ±0.04 mm s^{-1}. [d] Full width at half height. [e] Correlation coefficient for stated number of data points.

$Me_3SnO_2P(OPh)_2$ (73 Hz), which is postulated to be five-coordinated in solution [16]. The magnitude of these couplings is substantially higher than for tetrahedrally coordinated tin (e.g. Me_3SnCl in $CDCl_3$, 58.5 Hz [17]) and is generally held to be due to an increase in *s*-character in the Sn–C bonds concomitant with sp^3 to sp^2 rehybridisation within the framework of a *trans*-X_2SnR_3 geometry about tin. Five-coordinate tin surrounded by a *cis*-X_2SnR_3 ligand stereochemistry shows $^2J(^{119}Sn–C–^1H)$ coupling similar to that for four-coordinate tin e.g. Me_3Sn-(ON.Ph.CO.Ph), which is known to adopt a *cis*-O_2SnMe_3 structure in the solid state [18], $^2J(^{119}–Sn–^1H)$ 54 Hz [19]. These results concur with the postulates made on the

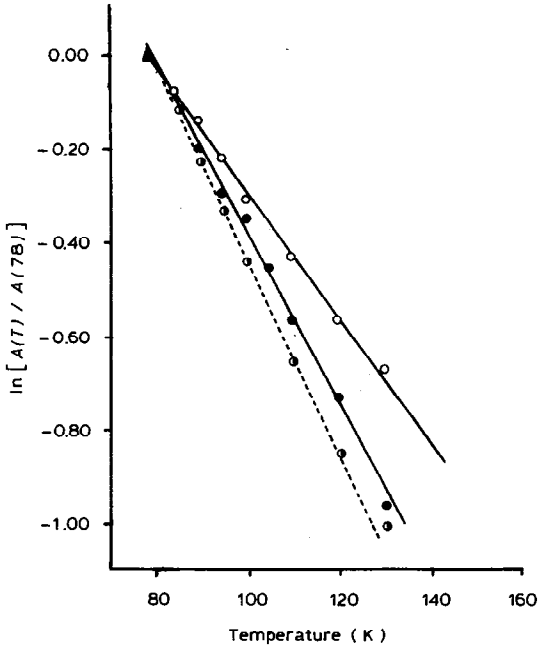


Fig. 1. Variable-temperature ^{119}Sn Mössbauer spectroscopic data for Me_3Sn(DPPA) (◑), Ph_3Sn(DPPA) (●) and Ph_3Sn(TEPA) (○). The point (▲) (78, 0.00) is common to all plots.

basis of the infrared data and on the assumption that a polymeric structure would either be too insoluble for NMR study or otherwise show some concentration dependence in the coupling constant magnitude, we rationalise these data in terms of cyclic, oligomeric species in solution.

Confirmation of the *trans*-O_2SnR_3 geometry adopted by the title compounds can be found in the Mössbauer data (Table 5). Isomer shift (*IS*) data are all typical of tin in the +4 oxidation state, while the enhanced quadrupole splitting values (3.38–3.91 mm s^{-1}) are greater than expected for tetrahedral (1.00–2.40 mm s^{-1}) or five-coordinated *cis*-X_2SnR_3 (1.70–2.40 mm s^{-1}) and are typical (3.00–4.00 mm s^{-1}) of a *trans*-X_2SnR_3 coordination about the metal [20]. *QS* data for analogous organophosphorus ligands ($H_2PO_2^-$ [15], $Me_2PO_2^-$, $(C_6H_{13})_2PO_2^-$ [13], $(PhO)_2PO_2^-$ [16] and $Ph(PhO)PO_2^-$ [21]) are in good agreement with those reported here.

The conclusions which we draw from the collective spectroscopic data are that all six compounds prepared adopt five-coordinate *trans*-O_2SnR_3 geometries, which are maintained in solution by the soluble tri-methyl-, butyl, and cyclohexyltin compounds. These latter four compounds are therefore most probably cyclic oligomers, as has been demonstrated to be the case in the hexameric $[Ph_3SnO_2P(OPh)_2]_6$ [22], but the molecularity of these species is uncertain. The two triphenyltin compounds, Ph_3Sn(DPPA) and Ph_3Sn(TEPA), are insoluble in common organic solvents and on this basis are more likely to be chain polymers than oligomers.

Further insights into the lattice structure of organotin compounds can be gained by studies of the temperature dependence of the recoil-free fraction, $f(T)$, and data for three compounds [Me_3Sn(DPPA), Ph_3Sn(DPPA) and Ph_3Sn(TEPA)] are shown in Fig. 1. Since:

$$f(T) = \exp\left[-\langle x(T)^2\rangle\right]/\lambda\!\!\!^{-2} \tag{3}$$

$$\frac{df(T)}{dT} = \frac{d}{dT}\exp\left(-6E_R T/k\theta_D{}^2\right) \tag{4}$$

where $\langle x(T)^2\rangle$ is the mean square amplitude of vibration of the tin, $\lambda\!\!\!^{-}$ the wavelength of the Mössbauer transition divided by 2π, E_R the Mössbauer recoil energy and θ_D the Debye temperature of the lattice, and, for 'thin' absorbers $A(T)$, the spectral area, and $f(T)$ are linearly related, then plots of $\ln[A(T)/A(78)]$ vs. T are linear. Normalisation of the data to 78 K is merely to facilitate intersample comparison. The slope of these plots, $a = -d\ln A/dT$, reflects the degree of lattice association, with non-associated lattices comprising discrete monomer, dimer, trimer etc. units having less rigid lattices (larger a) than those containing polymeric species, unless the polymer is severely coiled and thereby fails to restrict the vibrational motion of the Mössbauer atom [23,24]. The strongly temperature dependent Mössbauer spectrum for Me_3Sn(DPPA) (10^2a 2.11 K^{-1}) is consistent with a lattice consistent of non-interacting oligomers and can be compared to data for the soluble form of Me_3SnO_2CH ($10^2a = 1.90$ K^{-1} [1,25]) which is believed to be a cyclic species, possibly trimeric [26]. A similarly high a value for Ph_3Sn(DPPA) ($10^2a = 1.84$ K^{-1}) could also reflect an oligomeric species, but if the compound's insolubility is taken as evidence for lattice association, then this data is better interpreted in terms of a Class 3 [23] or 'S'-shaped polymer. The coiling of the polymer arises in part from the angular demands of the –OPO-bridging unit and in part minimisation of steric interactions between R groups bonded to tin and those

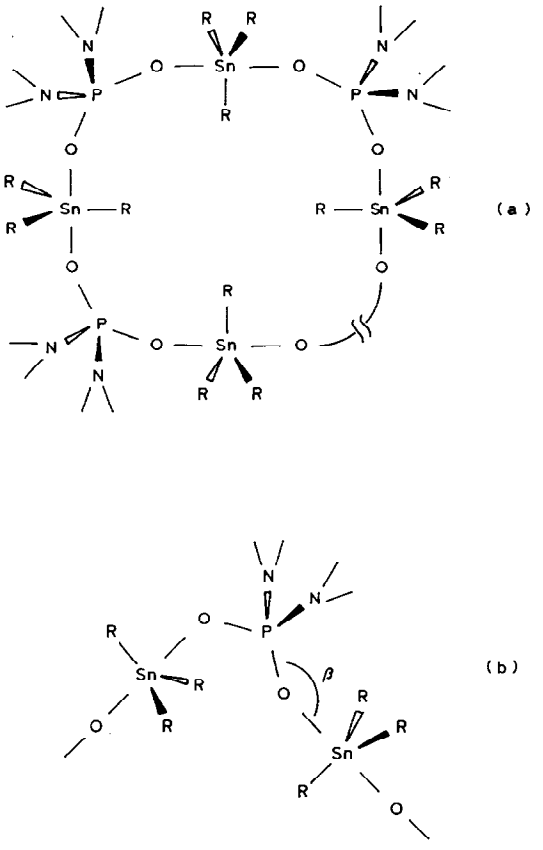


Fig. 2. Proposed structures for (a) soluble and (b) insoluble triorganotin phosphorodiamidates. The discontinuity in the cyclic structure reflects the uncertainty in the molecularity of these units.

bonded to phosphorus. Since Ph_3Sn(TEPA) is also polymeric by similar reasoning, the reduced value for 10^2a (1.33) suggests a more linear polymer i.e. more closely resembling a Class 2 or zig-zag spacial disposition of the polymer backbone [23], apparently arising from the smaller steric demands of the flexible C_2H_5 groups of the amide. We have observed a similar trend for Ph_3SnO_2CR where X-ray data confirm the more linear character in the formate polymer (R = H, $10^2a = 1.15\ K^{-1}$) than the acetate ($R = CH_3$, $10^2a = 1.91\ K^{-1}$) [1,8], as reflected in the β-angle (cf. Fig. 2b) which is 123.1, 125.5 and 142.7° for the two carboxylates respectively.

Conclusions

Spectral data show that triorganotin derivatives of phosphorodiamidic acids adopt a *trans*-O_2SnR_3 in both solid and solution phases. On this basis, soluble derivatives are assigned cyclic oligomeric structure (Fig. 2a), while the insoluble triphenyltin derivatives are polymeric (Fig. 2b). Variable-temperature Mössbauer spectroscopic data suggest that polymeric Ph_3Sn(TEPA) is constructed in a more linear fashion than Ph_3Sn(DPPA) polymer.

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